

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comment regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE May 15, 1997		3. REPORT TYPE AND DATES COVERED Final Progress - 4/1/94-3/31/97	
4. TITLE AND SUBTITLE DESIGN SYNTHESIS AND THEORY OF ION TRANSPORT IN A NEW CLASS OF SOLID POLYELECTROLYTES				5. FUNDING NUMBERS DAAH04-94-G-0066	
6. AUTHOR(S) M. A. RATNER AND D. F. SHRIVER					
7. PERFORMING ORGANIZATION NAMES(S) AND ADDRESS(ES) Northwestern University Department of Chemistry 2145 Sheridan Road Evanston, IL 60208-3113				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211				10. SPONSORING / MONITORING AGENCY REPORT NUMBER ARO 31499.8 -CH	
11. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.					
12a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.				12 b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) Polyelectrolytes, where anions are covalently bonded to the backbone have unit transference number for cations and are therefore, attractive for high energy density batteries. In this project, we prepared new polyelectrolyte materials and modeled the behavior of polyelectrolytes, to understand differences between polyelectrolyte conduction and polymer/salt complex electrolyte conduction. Major results include: <ol style="list-style-type: none"> 1. Reduction of the basicity of the anion in a polyelectrolyte by the development of aluminosilicate polyelectrolyte materials. 2. Development of nanocomposite polyelectrolytes, consisting of a polymer intercalated into clay materials. Demonstration that conduction in these materials is limited both by tortuosity effects and by the inherent mobility of the ion in the polymer. 3. Modeling demonstrates clearly that polyelectrolyte conduction will be reduced compared to polymer/salt complex electrolyte production, both because of the lack of anion mobility and because of higher average barriers due to rigidity of the polyanionic structure. We suggested a number of structural modifications that are likely to increase polyelectrolyte conduction. 					
14. SUBJECT TERMS Polymer electrolyte, polyelectrolyte, battery materials				15. NUMBER OF PAGES 8	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL		

DESIGN, SYNTHESIS AND THEORY OF ION TRANSPORT
IN A NEW CLASS OF SOLID POLYELECTROLYTES

FINAL PROGRESS REPORT

FOR PERIOD COVERING

APRIL 1, 1994 - MARCH 31, 1997

M. A. RATNER AND D. F. SHRIVER

MAY, 1997

U. S. ARMY RESEARCH OFFICE

GRANT NUMBER: DAAH04-94-G-0066

NORTHWESTERN UNIVERSITY

EVANSTON, IL 60208

APPROVED FOR PUBLIC RELEASE;

DISTRIBUTION UNLIMITED

THE VIEWS, OPINIONS, AND/OR FINDINGS CONTAINED IN THIS
REPORT ARE THOSE OF THE AUTHOR(S) AND SHOULD NOT BE
CONSTRUED AS AN OFFICIAL DEPARTMENT OF THE ARMY
POSITION, POLICY, OR DECISION, UNLESS SO DESIGNATED BY
OTHER DOCUMENTATION.

19970819 099

A. Statement of the Problem Studied

The two goals of this research were to prepare improved polyelectrolyte materials for cation conduction in secondary batteries, and to model the mechanistic bottlenecks to increased conduction, that limit power density in the final batteries.

Solutions of these two problems is crucial if advanced batteries based on polyelectrolytes are to be developed. Such batteries would have both high energy density and high power density, in addition to the other advantages of polymer-based batteries (stability, low cost, light weight, dimensional variability, safety, environmental compatibility).

B. Summary of Most Important Results

We feel that this research project has been extremely successful. Major accomplishments include:

1. Synthesis of new, single-phase polyelectrolyte materials based on reduced basicity an ionic centers. For example, in aluminosilicate structures, the effective basicity of the aluminate center can be reduced by inserting a silicon in place of a carbon beyond the first oxygen site. This reduced basicity results in less effective ion pairing, and therefore in higher cationic mobility and conductivity.
2. Preparation of composite polyelectrolyte materials, consisting of alkaline montmorillonite clays filled with a polymer such as polyphosphazene. These materials exhibit unit transference number for cations, dimensional and structural stability, and relatively high conduction. This conduction is limited both by the inherent mobility of the ion in the polymer, and by tortuosity effects due to particle size of the clays. Reduction of clay particle sizes reduces the tortuosity impediment and results in higher bulk reduction.

3. Demonstration of the effect of added complexing agents such as cryptands in increasing polyelectrolyte conduction, due to reduction of ion clustering and pairing.
4. Demonstration that increased dielectric constant of the polymer can indeed increase ionic conductivity, but that the fluidity of the polymer remains the dominant factor. Polycarbonates, therefore, are not a productive pathway, because their relatively high electric constant is more than balanced by their higher glass transition temperatures.
5. Demonstration based on mechanistic modeling that polyelectrolyte conduction will generally be lower than polymer/salt complex conduction, although the unity transference number for cations provides a substantial practical advantage in reducing salt polarization. Conduction drop in polyelectrolytes is due both to the lack of contribution from anions, and to the increased cation trapping, due to fixed, rather than mobile, counter-charge. Suggestions for structures to enhance polyelectrolyte conduction, both by reduced basicity and by increased flexibility of the anion tether, follow from these simulations.

The attached two figures are demonstrative of the findings of this research. Figure 1 shows a cartoon of the structure of a montmorillonite clay/sodium polyphosphazene composite electrolyte. In this case, the clay particles are flake-like in geometry, so that there is a tortuosity penalty for conduction perpendicular to the film, as opposed to parallel to the film. The activation energy for conduction shows clearly that the temperature dependence is dominated in both cases by the same factors (the slopes are the same), arising from the inherent mobility of the ion in the polymer host. The prefactors differ because of tortuosity.

Figure 2 shows the results of dynamic percolation studies of polyelectrolyte

materials, compared to analogous polymer/salt complex materials. The reduced conduction arises, as stated above, both from trapping of the cation and from the missing anion contribution. The effects that facilitate conduction in complex materials (lower glass transition temperature, reduced ion pairing) also increase cation conduction in polyelectrolytes.

Based on these observations, we believe that there are a number of very promising avenues for improved polyelectrolytes: these avenues will include flexible polyelectrolyte structures to reduce cation trapping, composite polyelectrolyte structures to increase interfacial conduction and provide a conductivity increment from polarization effects, and further reduction in local basicity arising from controlled structures in the polyelectrolyte. These are topics for future research in our laboratory.

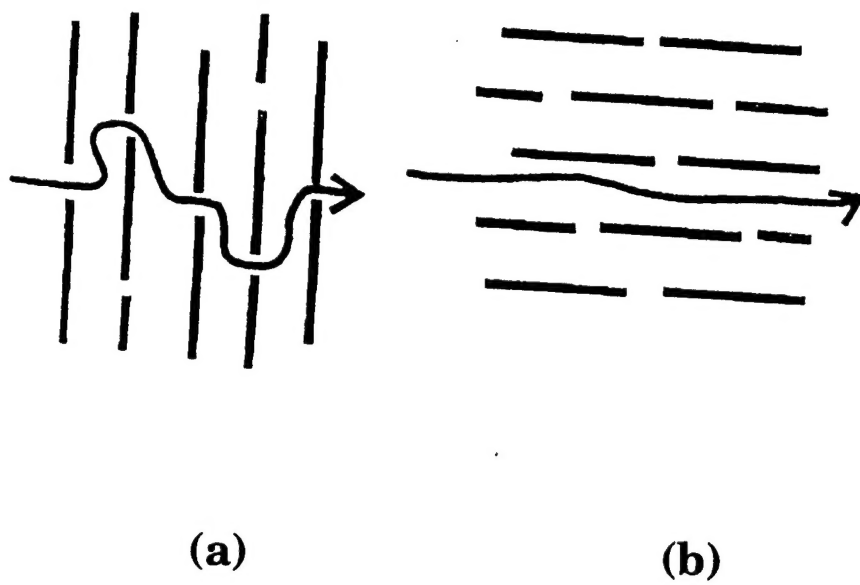


Figure 1: Schematic illustration of ion transport (a) perpendicular and (b) parallel to montmorillonite layers in montmorillonite polymer composites.

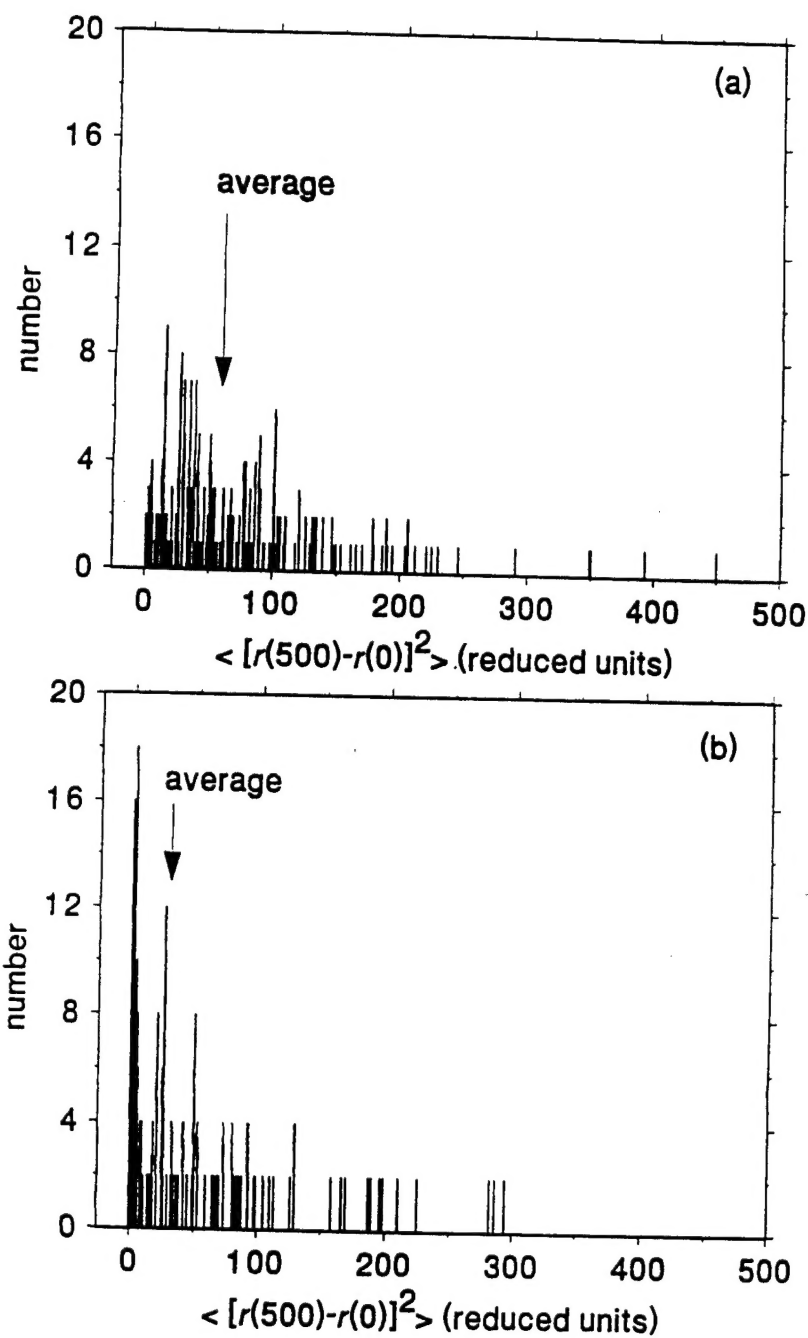


Figure 2: Dynamic percolation of (a) polymer salt complex
(b) polyelectrolyte

C. Publications

"Conductivity and Dielectric Constant of PPO & PPO-based Solid Electrolytes from DC to 6 GHz", A. L. Tipton, M. C. Lonergan, M. A. Ratner, D. F. Shriver, T.T.Y. Wong and K. Han, *J. Phys. Chem.*, **8**, 4148-4154 (1994).

"Highly Concentrated Salt Solutions: Molecular Dynamics Simulations of Structure and Transport", V. A. Payne, M. Forsyth, M. A. Ratner, D. F. Shriver and S. W. de Leeuw, *J. Chem. Phys.*, **100**(7), 5201 (1994).

"Ionic Diffusion in dynamically-Disordered Materials: Motion on a Renewing, Percolative Lattice", M. C. Lonergan, A. Nitzan and M. A. Ratner, *J. Molec. Liquids*, **60**, 269-288 (1994).

"Conduction in Polymers: Dynamic Disorder Transport", A. Nitzan and M. A. Ratner, *J. Phys. Chem.*, **98**, 1765 (1994).

"Dipole Time Correlation Functions of the Stockmayer Fluid in the Microcanonical and Canonical Ensembles", V. A. Payne, M. Forsyth, J. Kolafa and M. A. Ratner, *J. Phys. Chem.*, **97**, 10478 (1994).

"Aluminosilicate/Polyethylene Glycol CoPolymers: A New Class of Polyelectrolytes", G. C. Rawsky, T. Fujinami and D. F. Shriver, *Chem. Mater.*, **6**, 2208 (1994).

"The Mechanism and Modeling of Conductivity in Polymer Electrolytes", M. C. Lonergan, D. F. Shriver, A. Nitzan, M. A. Ratner, *Proc. Mater. Res. Soc. Symp., Solid State Ionics IV*, Vol. 369, G. Nazri, J. Tarascon and M. Schreiber, eds., p. 245 (1995).

"Dynamically Disordered Hopping Glass Transition, and Polymer Electrolytes", M. C. Lonergan, A. Nitzan, M. A. Ratner, and D. F. Shriver, *J. Chem. Phys.*, **103**(8), 3253 (1995).

"Cryptand Addition to Polyelectrolytes: A Means of Conductivity Enhancement and a Probe of Ionic Interactions", M. C. Lonergan, M. A. Ratner, and D. F. Shriver, *J. Am. Chem. Soc.*, **117**, 2344 (1995).

"Ion Clustering in Molecular Dynamics Simulations of Sodium Iodide Solutions", V. A. Payne, J. H. Xu, M. Forsyth, M. A. Ratner, D. F. Shriver and S. W. de Leeuw, *Electrochim. Acta*, **40**, No. 13,14, 2087 (1995).

"Development of Aluminosilicate Polyelectrolytes for Solid-State Battery Applications", G. C. Rawsky, K. J. Henretta, R. J. Lowrey, D. F. Shriver and S. Vaynman, *Proc. Mater. Res. Soc. Symp., Materials for Electrochemical Energy Storage and Conversion-Batteries Capacitors and Fuel Cells*, Vol. 393, D. H. Doughty, B. Vyas, T. Takamura, J. R. Huff, eds., p189-194 (1995).

Charge Transport Properties of a Partially Reduced V_2O_5 Xerogel Intercalated with a Polymer Electrolyte", J. A. Thomas, G. M. Kloster, D. F. Shriver and C. R. Kannewurf, in Materials for Electrochemical Energy Storage and Conversion-Batteries, Capacitors and Fuel Cells, D. H. Doughty, B. Vyas, T. Takamura, R. Huff, eds.; *Mater. Res. Soc. Symp. Proc.*, Vol. 393, 131 (1995).

"Simulations of Structure and Transport in Polymer Electrolytes", V. A. Payne, M. C. Lonergan, M. Forsyth, M. A. Ratner, D. F. Shriver, S. W. de Leeuw, J. W. Perram, *Solid State Ionics*, 81, 171-181 (1995).

"Synthesis, Characterization, and AC-impedance Measurements of New Polyphosphazene-Clay and Cryptand-Clay Intercalates", J. C. Hutchison, R. Bissessur and D. F. Shriver, Preprint, Div. of Polymeric Mat. Sci. and Engg., 73, (1995).

"New Polyphosphazene-Clay and Cryptand-Clay Intercalates", J. C. Hutchison, R. Bissessur and D. F. Shriver, Chapter 18 in Nanotechnology: Molecularly Designed Materials, ACS Symp. Series 622, G. M. Chow and K. E. Gonsalves, eds.; p262-272 (1996).

"Rational Design of Novel Polyelectrolytes: Aluminosilicate/Poly(Ethylene Glycol) Copolymers", G. C. Rawsy and D. F. Shriver, in *Metal Containing Polymeric Materials*, C. U. Pittman, C. E. Carraher, B. M. Culbertson, M. Zeldin and J. E. Sheets, eds., Plenum Publishing, 383 (1996).

"Conductivity Anisotropy of Polyphosphazene-Montmorillonite Composite Electrolytes", J. C. Hutchison, R. Bissessur, and D. F. Shriver, *Chem. Mater.*, 8, 1597-1599 (1996).

"Ionic Conductivity in Poly(diethylene glycol-carbonate)/Sodium Triflate Complexes", M. Forsyth, A. L. Tipton, D. F. Shriver, M. A. Ratner, *Solid State Ionics*, accepted.

D. Personnel Supported

D. F. Shriver and M. A. Ratner (Co/PI's)

Abraham Nitzan - Collaborator on project/visiting professor

Benjamin Vekhter - Research Fellow

Leonid Son - Postdoctoral Fellow

Jeremy Schofield - Postdoctoral Fellow

Mark C. Lonergan Ph.D. completed 1994.

Vilia A. Payne Ph.D. completed 1994.

William Davis - Graduate Student

J. Chris Hutchison - Graduate Student

Yi Mao - Graduate Student

Glenn Rawsy - Graduate Student

Xiang Wei - Graduate Student